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Evaluation of ozone-based oxidation and solar advanced oxidation treatment of greywater

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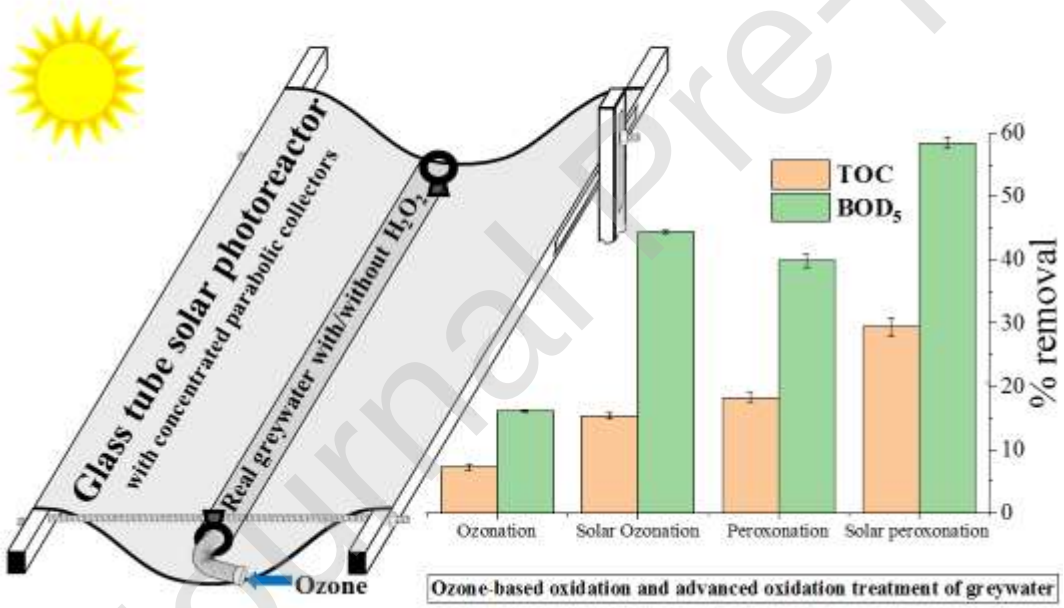
Graphical abstract



Highlights

- Solar AOPs effectively degraded organic matter in Jordanian greywater.
- Solar excitation increased degradation rates for ozone and peroxonation.
- Solar peroxonation reduced the TOC of GW by 59% with 3 hours.

Reclaiming non-conventional water sources such as greywater is gaining more attention in the light of current and expected water shortage due to the global trend of continued population growth, urbanization, and the impact of climate change. In this work, the degradation of organic matter measured as total organic carbon (*TOC*) and biochemical oxygen demand (BOD_5) in real greywater samples using different ozone-based oxidation and solar advanced oxidation treatments was investigated in a custom-built glass tube reactor combined with a concentrated parabolic collector (CPC). The evaluated processes included ozonation (O_3), solar ozonation (O_3/solar irradiation), hydrogen peroxide oxidation (H_2O_2), hydrogen peroxide under solar irradiation (H_2O_2/solar irradiation), peroxonation (H_2O_2/O_3), and solar peroxonation (H_2O_2/O_3/solar irradiation). Combining different treatment methods with/without exposure to solar irradiation enhanced overall treatment efficiency. The efficiency of the examined processes followed the order: solar peroxonation > solar ozonation > peroxonation > ozonation, while the other processes showed a negligible effect. The highest *TOC* reduction (58.6%) was observed using solar peroxonation at 41.7 mg O_3/min and 0.2 H_2O_2/O_3 molar ratio; the highest BOD_5 reduction (29.4%) was observed using solar peroxonation at 41.7 mg O_3/min and 0.4 H_2O_2/O_3 molar ratio. We conclude that low-cost advanced oxidation technologies can be effective to remove organic materials providing efficient greywater remediation for reuse applications.

Keywords: solar, greywater, ozonation, peroxonation, advanced oxidation processes

1. Introduction

Nearly half of the world's population are living in a potential water-scarce area for at least one month per year [1], with around 1.76 billion people living in regions facing drastic water shortage [2]. Whilst current water shortage is more crucial in developing countries [3], some developed countries, such as Australia and Japan, are also suffering from the same problem [4]. It has been predicted that water shortage will become more severe in future, based on the global trend of continued population growth and urbanization, in addition to the many impacts of climate change [5].

The significance of the current and predicted water shortage in the context of sustainable development and the availability of new technologies has brought more attention to the potential to utilize non-conventional water sources [6]. Reclaiming greywater (GW), which represents 50 – 75 percent of household water consumption [7], offers great potential to provide a local source of water for reuse [8]. GW is defined as the untreated domestic wastewater excluding the wastewater generated from toilet and, in most cases, the kitchen [8]. Reclaimed GW can be considered for a range of non-potable applications for both indoor or outdoor uses such as toilet flushing, irrigation, and washing vehicles [9]. Reuse could save from 40% up to 70% of household freshwater consumption [10], which consequently reduces the volume of generated wastewater and minimizes potential for water source pollution [11]. The quality and quantity of domestic GW are both affected by unlimited factors such as; the GW source, number and age distribution of residents occupying the house, in addition to their lifestyles and income level [12].

In Jordan, practices to separate and collect GW are more common in villages and rural areas [13], where the GW is mainly used, without any treatment, for irrigation [14]. To control the quality for GW for reuse, Jordan Standards and Metrology Organization (JSMO) issued the second edition of GW standard JS1776:2013 in 2013, considering non-potable GW reuse for irrigation and toilet flushing [15]. Although use of reclaimed GW for non-potable applications reduces the treatment requirements [16], GW still need to be treated from environmental and health points of view [17], according to its physico-chemical characteristics and the recommended standard [12].

GW typically contains a high BOD_5/COD ratio [12], lacks macro or trace nutrients [18] and contains a range of bio-recalcitrant compounds [19], and coupled with the variations in production rate and organic load [20] provides a significant challenge for biological treatments - especially for low volume, distributed reuse applications [21]. On the other hand, AOPs such as UV/H_2O_2, O_3/H_2O_2,

UV/O_3, TiO_2/UV, and photo-Fenton, produce hydroxyl radicals ($OH^{\bullet}$) in sufficient quantity to oxidize pollutants in water [16] representing a practical complementary treatment option for GW remediation. The advantages of AOPs over biological and other 'traditional' treatment methods include (i) AOP's destroy pollutants rather than transferring them to another phase [16], (ii) they can oxidize a wide range of materials without restrictions to specific compounds [22], and (iii) AOPs can effectively disinfect water [23].

Despite the long list of GW treatment methods and a similar long list of advanced oxidation processes (AOPs) with the potential to remediate water and wastewater, a limited number of studies have considered the application of single or combined AOPs specifically for GW treatment. TiO_2 photocatalysis has gained attention [5], but studies on ozone-based AOPs which utilize solar irradiation are limited. Whilst ozone itself has been widely used in water and wastewater treatment, for remediation of color, taste, odor and disinfection [24], it is not recommended as a standalone process for organic content reduction [25]. Enhancing O_3 efficiency and suitability through combination with solar irradiation (solar ozonation) [26-28], hydrogen peroxide (peroxonation) [29, 30] or with both hydrogen peroxide and solar irradiation (solar peroxonation) [28] offers promise for remediation of domestic [26, 29] and industrial wastewaters [30, 31] and landfill leachate [28, 32]. Nonetheless, large number of published ozone-based AOP studies have been carried out using a simulated solar source [26, 27] and/or simulated synthetic wastewater [26, 27, 29].

The study forms part of a larger body of work to co-develop sustainable GW re-use systems with local communities in Jordan; in this paper, we focus on the implementation of a simple low-cost photoreactor to study solar enhancement of ozone-based AOPs - solar ozonation and solar peroxonation (H_2O_2/O_3) - for the removal of organic content from real GW sampled from homes in Jordanian cities.

2. Material and methods

2.1. Greywater selection and characteristics

In order to reduce the error associated with the variation in GW characteristics, initial samples were undertaken over a five month period from 4 houses in different Jordanian cities, the site at Irbid was selected for consistency in biological load and GW subsequently collected for experiments. As is traditional in the country, the GW collection system in this house was installed by the homeowner during the house construction ensuring only the wastewater generated from the laundry, hand washing basins and showers was collected by a series of pipes joining a main pipe connected to a

200 L collection tank. The GW collection tank was fitted with a level switch that turns on an electrical pump on when the tank is full providing irrigation of crops without treatment. The GW retention time in the collection tank was typically 48 hours. The average GW characteristics of this house during the monitoring period are summarized in Table 1 and compared to Jordanian standard JS1776:2013 (GW analysis was carried out in the Royal Scientific Society laboratories according to the international standards [33]).

2.2. Grey water collection and storage

GW samples were collected manually from the GW collection tank in a 20 L polyethylene container, transferred to the laboratory within 1-2 hours, and stored at 3-5℃ to minimize any changes that might occur in GW properties before the experiments. To ensure results from each technology could be accurately compared, each set of experiments was conducted with a single batch of the collected GW.

Table 1. Characteristics of the GW from Irbid and the Jordan GW standard

Parameter (in mg/l unless otherwise stated)	Jordan GW standard JS1776:2013 for different applications [15]			Measured
	Irrigating vegetables that are		Toilet	
	Eaten cooked	Eaten raw	flushing	Mean ± SD
BOD_5	60	60	< 10	347 ± 31.2
COD	120	120	< 20	380 ± 28.6
TOC	-	-	-	126.4 ± 13.2
TSS	100	100	< 10	45.3 ± 7.42
pH (-)	6-9	6-9	6-9	7.72 ± 0.14
NO_3	70	70	70	0.375 ± 0.12
Total nitrogen(TN)	50	50	50	24.1 ± 2.27
Turbidity (NTU)	-	-	<5	57.8 ± 3.52
E. coli ($CFU/100\ ml$)	10^4	10^3	< 10	$1.1\times10^4 \pm 1.89\times10^3$
Intestinal helminths egg (-)	< 1	< 1	< 1	0
Fat Oil and Grease (FOG)	8	8	8	8.8 ± 1.5
Cl^-	500	500	500	425.3 ± 22.57
SO_4^{-2}	500	500	500	114.1 ± 8.72
NO_2 as N				0.067 ± 0.08
Total phosphorous (TP)	15	15	15	1.36 ± 0.37
Conductivity (µS/cm)	-	-	–	724.6 ± 0.27

2.3. Experimental set-up

All experiments were carried out in a custom-built borosilicate glass tube photoreactor with concentrated parabolic collectors installed facing south at a 30° angle on the roof of the Faculty of Natural Resources and Environment at the Hashemite University, Jordan. The photoreactor was

designed and fabricated by the research team to ensure it was robust and suitable for rural geographical locations, and in particular considering low cost materials, simple construction techniques and flexibility in adjusting the inclination and the focal distance. The reactor layout and dimensions are depicted in Fig. 1. Each collector was made from polished stainless steel sheet type 304. The aperture width was set to 40 cm for all experiments, and the focal distance was determined at 8 cm from the center of the parabolic reflector using basic green laser ray-tracing experiments.

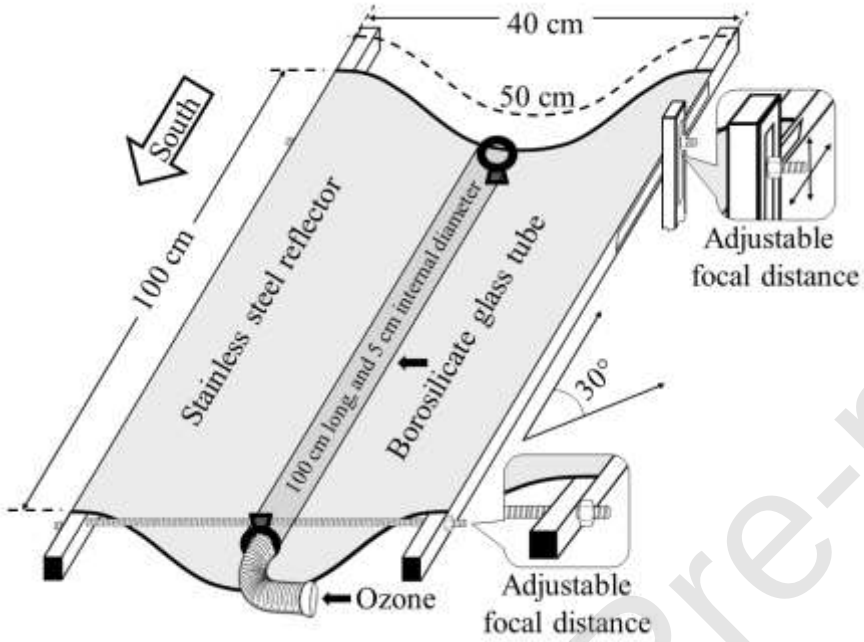


Fig. 1. Schematic of the glass tubes photoreactor with concentrated parabolic collectors.

In each experiment the volume of GW treated per tube was 1.5 L. The experiments under solar irradiation were carried out for 3 hours between 10:30 and 13:30 during May and June 2017. Figure S1 shows global radiation data taken from the photovoltaic Solar Station (LP02 pyranometer (Hukseflux Thermal Sensors, Netherlands)) at the Hashemite University with the hourly averaged global radiation measured on the hour at 11:00, 12:00, 13:00 and 14:00 each day during the experimental period. The incident radiation during the experiments was very consistent such that the average global radiation (AGR) between 10:00 and 14:00 during days of the solar experiments was 1.00 kW/m^2 ± 0.013 kW/m^2 (Max. 1.067 kW/m^2, Min. 0.939 kW/m^2). The average final water temperature of the treated GW was 37.71°C ± 2.79°C (Max. 41.60°C, Min. 34.01°C).

For experiments with no irradiation (dark experiments), the glass tubes were wrapped with aluminum foil. Depending on the purpose of the experiments, air or air with ozone were continuously fed at the

bottom of the tube reactor using ozone generator (OZ-3G, Ozonefac Ltd., china) with air input; the generator has variable outlet ozone concentration from 0 - 2.5 g/hr and constant air flow rate at 5 L/min. At regular intervals, samples (6 mL) were withdrawn for *TOC* measurement. For BOD_5 analysis, a 500 mL sample was taken from the initial greywater, with the same volume removed from the tubes and at the end of each experiment.

2.4. Analytical methods

The evaluation of mineralization was determined by measuring the total organic carbon (*TOC*) of GW samples rather than chemical oxygen demand (*COD*) in order to avoid the interference of H_2O_2 with *COD* measurement [34]. *TOC* was analyzed using Shimadzu 5000 *TOC*/V (Total Organic Carbon and Total Nitrogen Analyzer) with solid sample combustion unit SSM-5000A employing regular sensitivity Pt catalyst. The biodegradable organic content of the water was determined by measuring the biochemical oxygen demand (BOD_5) with BOD_5 EVO System 6 (VELP Scientifica, Inc). All BOD_5 samples were subjected to extended aeration for 15 min in the dark before BOD_5 measuring in order to remove any residue ozone that may interfere with BOD_5 measurements. All samples in this study were analyzed in triplicate unless otherwise stated.

2.5. Calculations

TOC and BOD_5 percentage of removal was calculated as follow:

$$TOC \text{ removal } \% = 100 \times \frac{TOC_0 - TOC}{TOC_0} \qquad \text{Eq. 1}$$

$$BOD_5 \text{ removal } \% = 100 \times \frac{(BOD_5)_0 - BOD_5}{(BOD_5)_0} \qquad \text{Eq. 2}$$

Where the (0) notation represents the initially measured values before the treatment.

The kinetics of *TOC* reduction was fitted using the pseudo-first-order rate equation as follow [35]:

$$\frac{d(TOC)}{dt} = k(TOC) \rightarrow ln\frac{(TOC)}{(TOC)_0} = kt \qquad \text{Eq. 3}$$

Where k represents the apparent rate constant (min^{-1}) and *t* the time (*min*).

The biodegradability was represented by the ratio of BOD_5 to *TOC* [36] as follow:

$$Biodegradability = \frac{BOD_5}{TOC} \qquad \text{Eq. 4}$$

The results shown in this study are the average of triplicate measurements, and the error bars represent the standard deviation from the mean.

3. Results and discussion

3.1. Control experiments

Two control experiments were performed where GW was aerated for 3 hours a) in the dark and b) under solar irradiation (Fig. 2). As can be observed, aeration in the dark had a minimal effect on the GW organic content and biodegradability; perhaps due to the presence of a small fraction of volatile organic compounds in the GW or the escape of volatile compounds in the early stage in the GW collection tank before the sample collection.

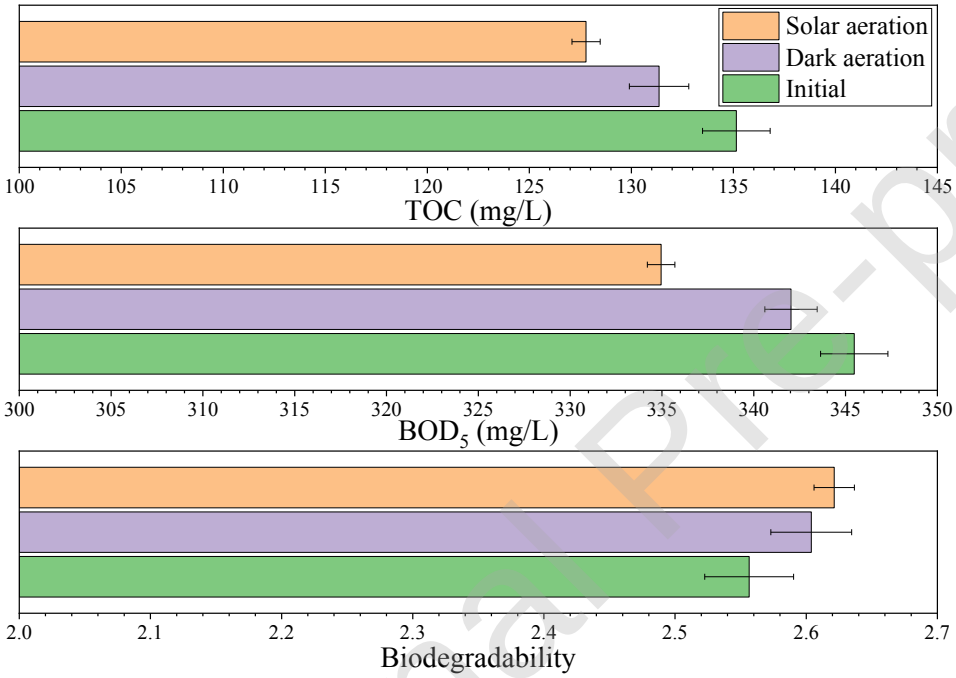


Fig. 2. Solar and dark aeration control experiments. Experimental time = 3 h; air flow rate = 5 L/min. AGR during solar aeration = 0.957 kW/m^2.

When GW was exposed to aeration coupled with solar irradiation, *TOC* and *BOD_5* were reduced by 5.4 % and 3.0 %, respectively. The low reduction in *TOC* and *BOD_5* values is likely attributed to the absence of the photosensitizers that can absorb radiated energy in the solar spectrum and initiate ROS production and subsequent organic pollutant mineralization [37]. One such photosensitizer, nitrate, which is plays a key role in solar treatment [37], was measured at very low concentrations in the GW (0.375 ± 0.12 mg/L). Similar findings of low organic matter photodegradation in different water sources have been reported [38]. For GW photodegradation, Chin *et al.* [39] observed no

reduction in *TOC* by direct photolysis using a low wavelength irradiation sources (15W UVC) lamps. In general, organic compound photodegradation is profoundly affected by a) the nature of pollutants in water, b) pollutants absorbance spectrum, and c) the employed light source wavelength and intensity [40]. According to the literature, organic compounds in water may go through a series of photo-induced reactions that may lead to, changes in molecular weight distribution (MWD) [41], complete degradation of particular compound [42], the formation of intermediates [43], transformation in aromaticity degree [41] or change in absorbance [39], but not necessarily to mineralization and significant change of organic content. The results above show small changes in BOD_5, suggesting minimal structural changes to the organics present in the GW.

3.2. Ozonation and solar ozonation

Ozonation and solar ozonation experiments were carried out by applying various ozone flow rates ranging from 0 to 41.7 mg O_3/min, flow rate as reported for previous treatment of GW [44] and wastewater studies [45].

As shown in Fig. 3, exposing GW to ozone enhanced treatment performance compared to aeration alone (zero ozone flow rate) either both dark or under solar irradiation. This enhancement is expected as ozone is not only a more potent oxidant than oxygen (E° = 2.07 V) [7] but also can attack the organic material through the generation of hydroxyl radicals from O_3 decomposition [46], and/or O_3 photolysis [47, 48]. The O_3 decomposition reactions are initiated by the hydroxide ions as follow ([49] and references therein):

$$3O_3 + OH^- \rightarrow OH^\bullet + O_3^{\bullet-} + 3O_2 \qquad \text{Eq. 5}$$

If pH < ≈ 8 $$O_3^{\bullet-} + H^+ \leftrightarrow HO_3^\bullet \rightarrow OH^\bullet + O_2 \qquad \text{Eq. 6}$$

If pH > ≈ 8 $$O_3^{\bullet-} \leftrightarrow O^{\bullet-} + O_2 \qquad \text{Eq. 7}$$

$$O^{\bullet-} + H_2O \rightarrow OH^\bullet + OH^- \qquad \text{Eq. 8}$$

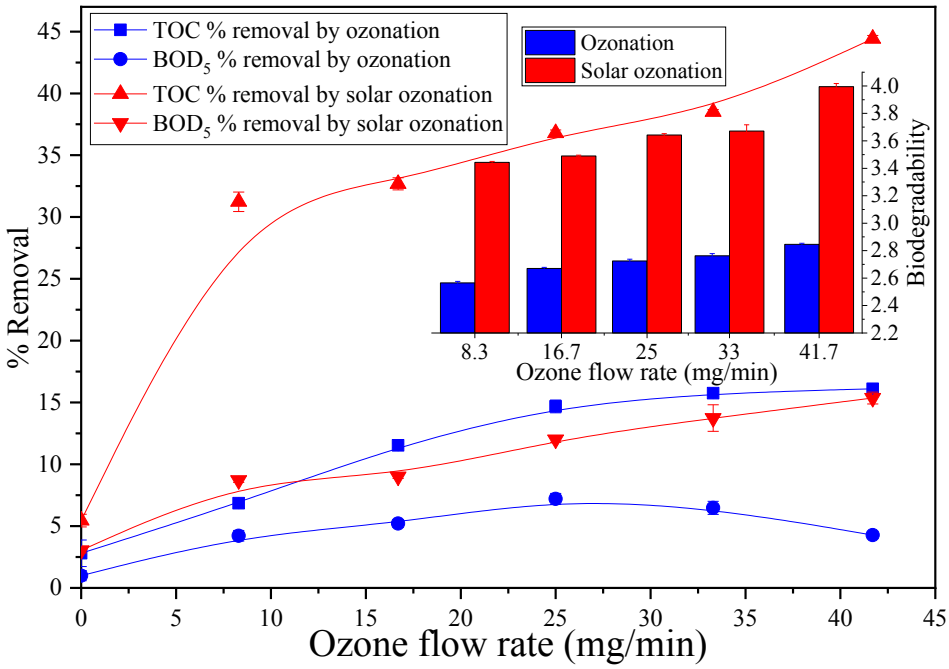


Fig. 3. *TOC* and *BOD*$_5$ removal in GW by ozonation and solar ozonation by different O_3 flow rates with inset showing resultant biodegradability. Experimental time = 3 h; air flow rate = 5 L/min. AGR = 1.016 kW/m^2 ± 0.042 kW/m^2.

The treatment performance was strongly enhanced under solar irradiation, a trend previously reported [45]. According to Oturan and Aaron [47], ozone can absorb energy in the range of 200 – 360 nm increasing the production of $OH^{\bullet}$ [48] and subsequent treatment efficiency (Eq. 9).

$$O_3 + H_2O + hv \rightarrow 2\,OH^{\bullet} + O_2 \qquad \text{Eq. 9}$$

Photolysis during solar ozonation is not considered to significantly affect the *TOC* given that carboxylic acid, which is the primary intermediate from ozonation, does not absorb radiation higher than 313 nm [35].

Regardless of the ozone flow rate in this study, only partial reduction in organic content was achieved (maximum 44.4% and 15.1% for *TOC* and *BOD*$_5$, respectively, by solar ozonation) a trend previously reported in the literature for ozonation [46, 50] and solar ozone treatment [35]. The enhancement in biodegradability, as shown in the inset of Fig. 3 can be considered in the light of the direct and indirect modes of action associated with ozone chemistry [51]. In the direct mode, ozone selectively oxidizes organic compounds that have nucleophilic moieties (such as; carbon-carbon double bond, aromatic rings, and specific functional groups) [46], and produces saturated intermediates (mainly carboxylic acids) with low reactivity toward ozone [35, 49]. This mode of ozone attack is expected to increase the *BOD*$_5$ rather than reduce the *TOC* (i.e. transforming the non-

biodegradable organic matter to biodegradable forms). On the other hand, the indirect attack by the hydroxyl radicals, generated from O_3 decomposition or O_3 photolysis, can completely mineralize organic compounds into CO_2 and H_2O [51]. As a result, the reduction in *TOC* is mainly attributed to oxidation by the limited number of hydroxyl radicals. In contrast, the change in the BOD_5 represents the net difference between the formation of the intermediates by direct O_3 oxidation and the mineralization of the biodegradable organics by the hydroxyl radicals. According to Gunten, the rate of intermediates formed by direct O_3 attack is higher than their rate of oxidation by the $OH^{\bullet}$ [49], which dictates that the reduction in the BOD_5 will be lower than that for *TOC*.

Unfortunately, increasing O_3 flow rate will not necessarily produce a greater concentration of hydroxyl radicals as ozone is reported to have an inhibitory effect at high dose [7], through scavenging the reactive hydroxyl radicals ($OH^{\bullet}$ E°= 2.8 V) [52] producing the less reactive hydroperoxyl radical ($HO_2^{\bullet}$ E°= 1.7 V) [53] according to Eq. 10 [7].

$$O_3 + OH^{\bullet} \rightarrow HO_2^{\bullet} + O_2 \qquad \text{Eq. 10}$$

Hydroxyl radical scavenging by ozone, and generation of the weak hydroperoxyl radicals, in addition to the accumulation of the intermediates during the ozonation process, could result in the decrease in *TOC* removal and the decline in BOD_5 observed at O_3 flow rates higher than 25 mg/min. Gracia and coworkers [54] observed such an effect with no more than 33% *TOC* reduction evident in their work using a very high O_3 dosage (4.5 g O_3/1 g *TOC*).

3.3. H_2O_2 and H_2O_2/solar irradiation

H_2O_2 is considered as a relatively inexpensive and environmentally friendly oxidant as it can dissociate into harmless products [55]. Even though it has a weak oxidation potential of 1.78 V [47], which limits its use for organic compounds degradation.

The efficiency of H_2O_2 for GW treatment, using up to 100 mg H_2O_2/L, was tested with and without solar irradiation, and no significant enhancement in the treatment performance was observed compared to the controls in Fig. 2 (results not shown). Reported studies regarding sole H_2O_2 efficiency in the treatment of different water pollutants classified the resultant effect as negligible [56], intermediate [57] and high [58].

H_2O_2 can be activated by energy within the 200 to 300 nm range generating hydroxyl radicals, according to Eq. 11 [47].

$$H_2O_2 + hv \rightarrow 2\,OH^{\bullet} \qquad \text{Eq. 11}$$

As such, H_2O_2 can be combined with high energy irradiation sources such as UVC [5], UV-ABC [59], VUV [60] and UVAB [61]. Previous studies regarding H_2O_2 photolysis (UV/H_2O_2) using short-wavelength light source have reported high *COD* or *TOC* removal efficiency, with reports using longer wavelengths finding similar efficiencies to those reported in this work [53, 56].

3.4. Peroxonation and Solar peroxonation

Peroxonation [47], often referred to as wet peroxide ozonation [62] and perozonation [37], couples O_3 with H_2O_2 for water treatment. In this study, we examine GW treatment efficiency by peroxonation (in the dark) and solar peroxonation (under solar irradiation), three O_3 flow rates (8.3, 25, and 41.7 mg O_3/min) in combination with H_2O_2 in different H_2O_2/O_3 molar ratios (ranging from 0 - 0.7) – in line with parameters from previous research [47, 63, 64]. The results of those experiments are represented in Fig. 4, by two-dimensional contour plots to find the optimal process conditions.

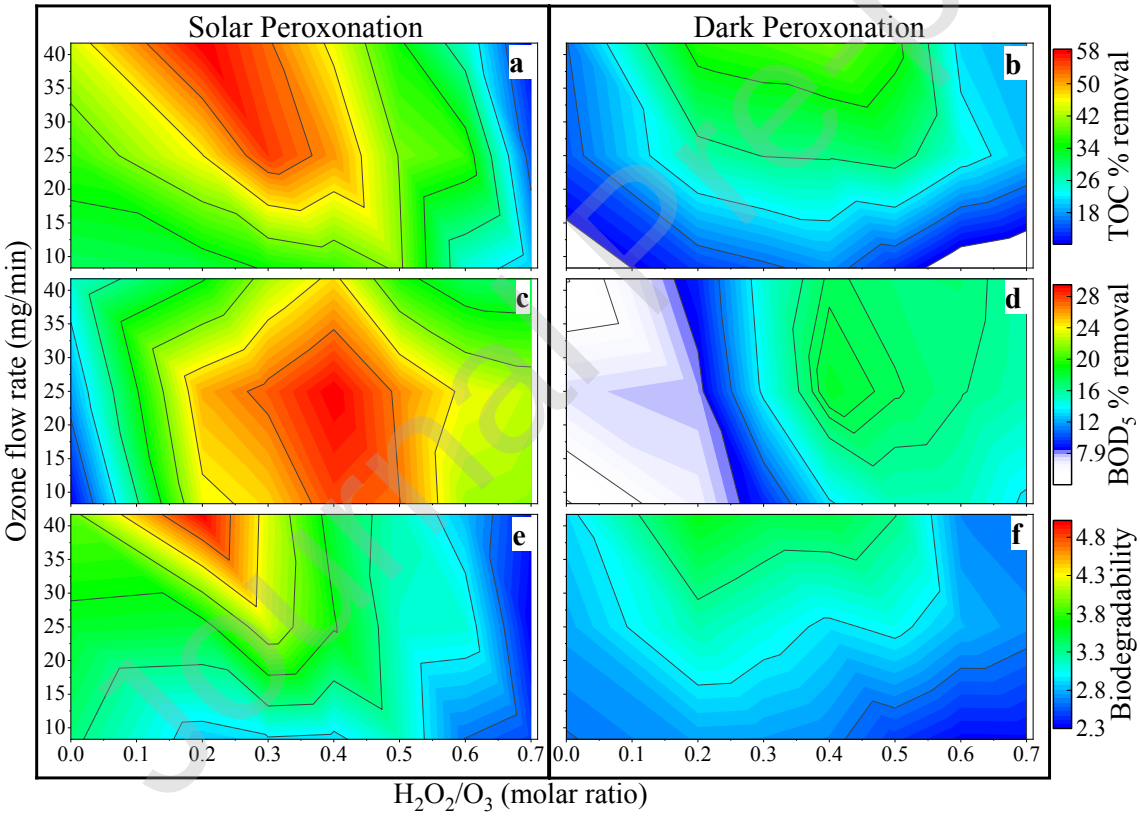


Fig. 4. *TOC* and *BOD*$_5$ percentage removal and biodegradability by solar peroxonation (left) and peroxonation (right) under different O_3 flow rates and different H_2O_2/O_3 molar ratios, ozone flow rate (8.3 - 41.7 mg/min), H_2O_2/O_3 molar ratio (0 - 0.7). Experimental time = 3 h; air flow rate = 5 L/min. AGR = 1.003 kW/m^2 ± 0.024 kW/m^2.

Coupling H_2O_2 with O_3 significantly enhanced treatment efficiency compared to ozonation alone. Similar findings have been reported in the literature [5, 62] and accredited to the increased concentration of hydroxyl radicals generated via Eq. 12 [62, 65].

$$2O_3 + H_2O_2 \rightarrow 2OH^{\bullet} + 3O_2 \qquad \text{Eq. 12}$$

It is noteworthy that the formation of the hydroxyl radicals in peroxonation (Eq. 12) is much faster than from ozone decomposition (Eq. 5 - Eq. 8) [50].

According to the literature, combining peroxonation with UV irradiation (UV peroxonation) can further enhance treatment efficiency through further generation of $OH^{\bullet}$ [5, 62]. Given the available solar wavelength range entering the reactor and the findings in the previous section, the increase in $OH^{\bullet}$ concentration during solar peroxonation could be attributed to O_3 photolysis but not to H_2O_2 photolysis. Consistent with findings in literature, solar peroxonation in this work intensified the *TOC* and BOD_5 reduction and therefore enhanced the GW biodegradability compared to dark peroxonation (Fig. 4).

One of the critical parameters in peroxonation and UV peroxonation processes is the H_2O_2 to O_3 ratio. It is well understood that excessive concentration of O_3 [7] or H_2O_2 [32]can quench the hydroxyl radicals and form the less reactive hydroperoxyl radicals (Eq. 13) [34].

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \qquad \text{Eq. 13}$$

In previous studies, a range of H_2O_2/O_3 molar ratios have been described as optimal for water treatment, such as 0.3 [65], 0.14 [64], 0.08 [66]; the largest recommended being 0.5 [63]. As can be seen from Fig. 4, we observed an optimal range for the ratio rather than a single value. As summarized in Table 2, the range being affected by the parameter of interest (*TOC*, BOD_5, or the biodegradability) and the O_3 flow rate.

Table 2. Optimum conditions in peroxonation and solar peroxonation treatment for *TOC* and BOD_5 reduction and for biodegradability.

	Peroxonation			Solar peroxonation		
Parameter of interest	*TOC* removal	BOD_5 removal	Biodegradability	*TOC* removal	BOD_5 removal	Biodegradability
Maximum value	9.83%	8.22%	.01	8.57%	9.4%	.65
O_3 flowrate (mg/min)						
Optimum range	3 - 41.7	0 - 33	3 - 41.7	5 - 41.7	.3 - 33	3- 41.7
Optimal value	1.7	5	1.7	1.7	5	1.7
H_2O_2/O_3 molar ratio						
Optimum range	.2 - 0.5	.4 - 0.5	.15 - 0.25	.2 - 0.3	.3 - 0.5	.10 - 0.50
Optimal value	.4	.4	.2	.2	.4	.2

For *TOC* reduction by peroxonation, effective treatment was observed within the range of H_2O_2/O_3 molar ratio (0.2 - 0.5) and a high range of O_3 flow rate (33 - 41.7 mg/min). In this region, hydroxyl radicals generated from O_3 decomposition (Eq. 5 - Eq. 8) and from O_3 reaction with H_2O_2 (Eq. 12) resulted in mineralization of organics. Outside this region, organic degradation is reduced by hydroxyl radical scavenging. Below the optimum ratio range, hydroxyl radical scavenging due to the extra O_3 (Eq. 10); however, above the range, scavenging results from extra H_2O_2 (Eq. 13).

For *TOC* reduction by solar peroxonation, the enhanced availability of hydroxyl radicals is expected to intensify the inhibition effect of H_2O_2 and shift the H_2O_2/O_3 ratio to values lower than 0.5.

According to Gunten, the rate of intermediate formation by direct O_3 attack is higher than their rate of oxidation by the $OH^{\bullet}$ [49], and therefore BOD_5 reduction favored low O_3 flow rate and middle-range H_2O_2/O_3 ratios.

3.5. Mineralization kinetics

Based upon the above results, four systems were selected for a study the *TOC* reduction kinetics: (i) ozonation with 41.7 mg O_3/min in the dark, (ii) solar ozonation with 41.7 mg O_3/min under solar irradiation, (iii) peroxonation with 41.7 mg O_3/min and 0.4 H_2O_2: O_3 molar ratio in the dark, and (iv) solar peroxonation with 41.7 mg O_3/min and 0.2 H_2O_2: O_3 molar ratio under solar irradiation (Fig. 5).

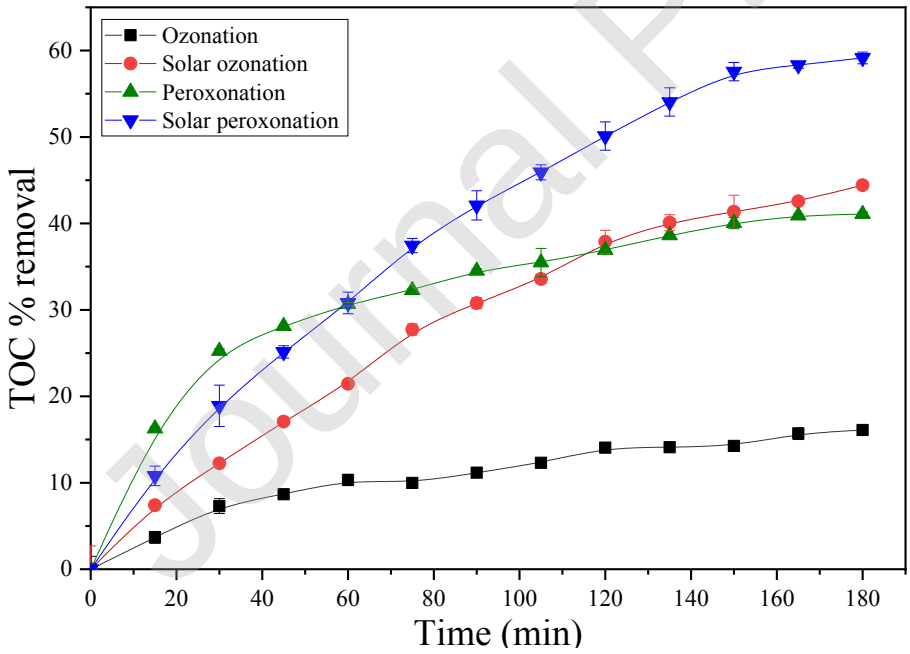


Fig. 5. Kinetics of *TOC* reduction by different treatment methods under the optimal conditions. Solar ozonation (AGR 0.973 kW/m^2), peroxonation at 0.4 H_2O_2/O_3 molar ratio, solar peroxonation at 0.2

H_2O_2/O_3 molar ratio (AGR 0.949 kW/m^2). All experiments at 41.7 mg O_3/min and air flow rate = 5 L/min.

TOC reduction in all experiments can be represented by the pseudo-first-order rate, whereas the experiments under solar irradiation fall into a single kinetic regime, and the dark experiments fall into two distinct kinetic regimes (from 0-30 min, and > 30 min) (Fig. 6).

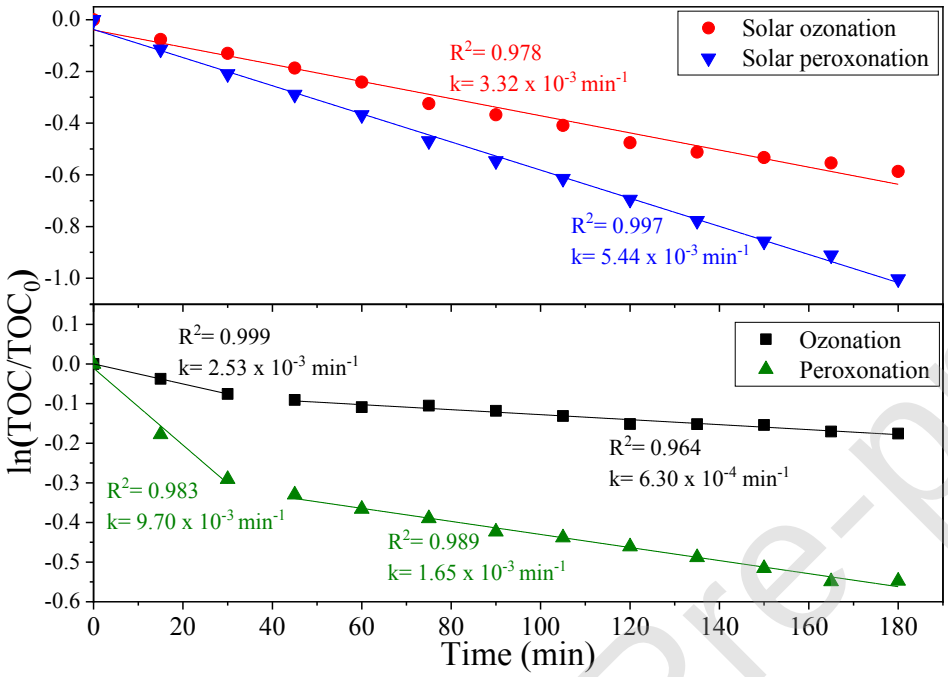


Fig. 6. Pseudo-first-order kinetics of *TOC* reduction by different treatment methods under the optimal conditions. Experimental conditions as shown in Fig. 5.

The theory behind the pseudo-first-order rate in ozone based treatment considers a steady rate of hydroxyl radicals formation by different means (i.e., O_3 decomposition, O_3 photolysis, and O_3 reaction with H_2O_2), and $OH^{\bullet}$ scavenging [49]. For experiments under solar irradiation (solar ozonation and solar peroxonation) O_3 introduced to the system is involved in $OH^{\bullet}$ formation, resulting in negligible remaining O_3 for $OH^{\bullet}$ scavenging. In contrast, in the dark experiments (ozonation and peroxonation), all O_3 introduced to the system, at the beginning of the experiment, is involved in $OH^{\bullet}$ formation, but when there is more O_3 in the system (after 30 min in this case), $OH^{\bullet}$ scavenging starts to be more dominant and a new steady rate starts to be established between $OH^{\bullet}$ formation and scavenging. To further investigate the previous $OH^{\bullet}$ formation and scavenging hypothesis, further experiments with lower O_3 flow rate were performed (Fig. 7) with one kinetic regime observed. Additionally, for a higher O_3 flow rate, a new kinetic regime is apparent. The first

regime duration can be positively correlated to O_3 flow rate, which indicates that *TOC* reduction is more a function of ozone exposure (O_3 flow rate × Time) rather than the time alone. Similar observations have been reported in literature [26].

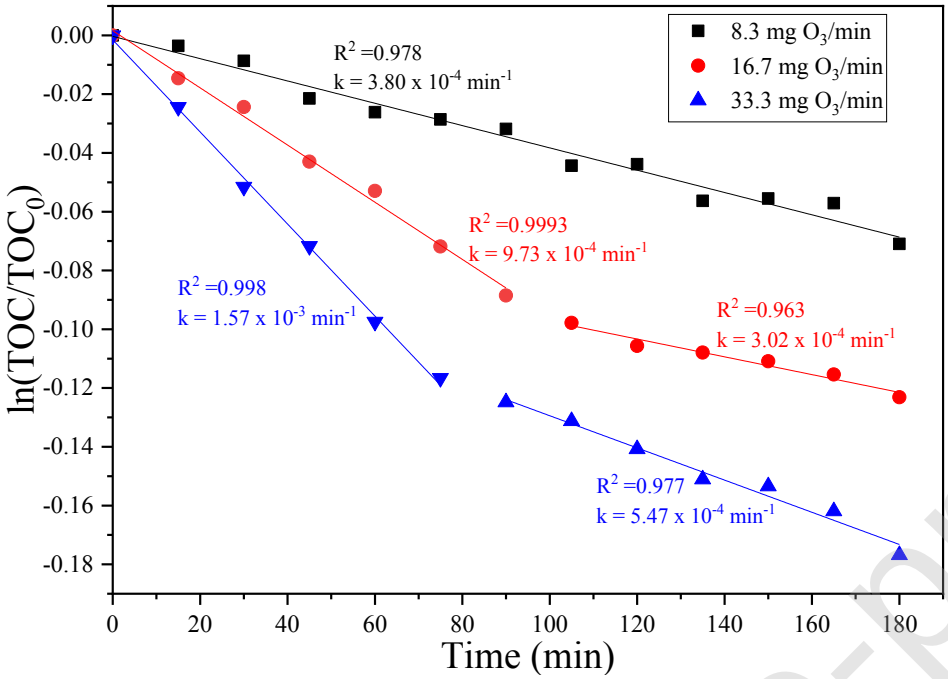


Fig. 7. Pseudo-first-order kinetics for ozonation at different O_3 flow rates. Air flow rate = 5 L/min.

4. Conclusion

A series of solar AOPs were shown to be effective the degradation of organic matter in greywater obtained from households in Jordan using a low-cost, concentrated parabolic collector reactor. Through analysis of the total organic carbon (*TOC*) and biochemical oxygen demand (BOD_5) the operating parameter ranges and kinetics for ozone-based oxidation and peroxonation advanced oxidation were deduced. All treatment methods were enhanced by solar irradiation, with solar peroxonation showing the highest *TOC* reduction (58.6%) (at 41.7 mg O_3/min and 0.2 H_2O_2/O_3 molar ratio) and the highest BOD_5 reduction (29.4%) (41.7 mg O_3/min and 0.4 H_2O_2/O_3 molar ratio). Although the organic load of the GW was significantly reduced, further work is required to increase both the kinetics and volumes of water treated before the solar AOP treatments could be coupled to the household GW recycling systems.

4.1. CRediT author statement

Dheaya Alrousan: Conceptualization, Methodology, Investigation, Resources, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization, Funding acquisition **Patrick Dunlop:** Validation, Formal analysis, Supervision, Project administration

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figure S1 Hourly averaged global radiation (measured on the hour at 11:00, 12:00, 13:00 and 14:00) each day during the experimental period (May and June 2017).